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THEORY OF BOUND STATES ASSOCIATED WITH n-TYPE

INVERSION LAYERS ON SILICON[*]

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Abstract

The ground state and two excited states of an electron bound
to a charged impurity located at the interface between silicon and
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the oxide has also been investigated.

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I. INTRODUCTION

The development of MOS devices has stimulated a great deal of interest in the basic properties of inversion layers at semiconductor boundaries. A number of these properties are influenced by the presence of impurities and their associated electronic bound states. We have investigated using a variational technique the ground state and two excited states of an electron bound to a bare charged impurity located at the interface between silicon (001) and silicon dioxide.

Theoretical investigations of the wave functions and binding energies of donor states localized at or near semiconductor surfaces without inversion layers have been carried out by Karpushin[1] and by Bell et al.[2] The effect of n-type inversion layers and electric sub-bands has been studied by Stern and Howard[3] for InAs and Si(001) surfaces. They considered the screening produced by the inversion layer charge carriers, but restricted their numerical results to the two-dimensional limit. In the present paper we eliminate the latter restriction, but neglect the effect of screening.

For the case of an n-type impurity at a semiconductor-oxide interface where the potential energy rises discontinuously to infinity, the ground state is, in hydrogen atom nomenclature, the $2p_o$ level.[2] In addition, the first excited states to which a transition might be observed in optical absorption are the $3d_{\pm 1}$ and $4d_{\pm 1}$ states. This result is due to Levine[4] who showed that a state cannot exist unless $\ell + m$ is an odd integer and that both ℓ and m must differ by ± 1 in an electromagnetic transition. Here we consider only the $3d_{\pm 1}$ excited states.

The binding energy of the impurity ground state which we
calculate is compared to the recent experimental data of
Hartstein and Fowler.[6]

II.   THEORETICAL DEVELOPMENT

We consider two contiguous, semi-infinite half-spaces,
one of p-type silicon and the other of SiO_2, with a common
boundary parallel to a (001) plane of the silicon. We
assume that the potential energy of an electron undergoes a
discontinuous jump as the electron passes from the silicon
into the SiO_2. This discontinuity in energy is about 3 eV[3];
however, we shall assume that the discontinuity is infinite and
that the electronic wave functions vanish at the boundary. In
the region of the inversion layer, there is an electric field
present which in general is a complicated function of the dis-
tance from the interface. To a good first approximation[3] one
can take the electric field to be constant, a procedure which we
adopt in this paper.

We assume that an impurity ion of charge +Ze is located
at the boundary between the silicon and the SiO_2. For this
situation, Karpushin[1] has shown that in the absence of an
external electric field the lowest lying bound states associated
with a (001) interface on silicon are primarily derived from the
energy ellipsoids whose major axes are perpendicular to the
interface. This situation continues to hold in the presence
of an electric field. We therefore consider only the ellipsoids

just mentioned. We also neglect intervalley interactions between the two ellipsoids perpendicular to the surface. Finally, we operate within the framework of the effective mass approximation.

In the light of the foregoing discussion, we employ the Hamiltonian

$$H = -\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) - \gamma\frac{\partial^2}{\partial z^2} + U(\vec{r}) + \frac{\delta}{z} + \chi\, \mathcal{E}z \tag{1}$$

where $\gamma = m_t/m_\ell$, $\delta = (\epsilon_2 - \epsilon_1)/4Z\epsilon_2$, $\chi = \hbar^4(\epsilon_1 + \epsilon_2)^3/4Z^3 m_t^2 e^5$, $\mathcal{E}$ is the external electric field, m_t and m_ℓ are the transverse and longitudinal effective masses, respectively, and ϵ_1 and ϵ_2 are the dielectric constants of the SiO_2 and silicon, respectively. In Eq. (1), energy is measured in units of the effective Rydberg, $Ry^* = 2m_t e^4 Z^2/\hbar^2(\epsilon_1+\epsilon_2)^2$ and length in units of the effective Bohr radius, $a_o^* = \hbar^2(\epsilon_1 + \epsilon_2)/2Z m_t e^2$. For the silicon-silicon dioxide system, $Ry^* = 42.3$ meV and $a_o^* = 21.8$ A. The potential energy $U(\vec{r})$ takes into account the interaction of the electron with the impurity ion and with the image of the impurity ion and also the screening of the impurity ion potential by electrons in the inversion layer. In the present paper, we neglect screening and take $U(\vec{r})$ to have the Coulomb form

$$U(\vec{r}) = -\frac{2}{r} \tag{2}$$

where $r = (x^2 + y^2 + z^2)^{\frac{1}{2}}$. The term involving δ in Eq. (1) represents the interaction of the electron with its own image. Our Hamiltonian consists of that of Karpushin with the addition of the electric field term.

We shall be particularly interested in the regime of large electric fields where the electric sub-band energies are large compared to the impurity binding energy. The problem is then analogous to the problem of an impurity in a high magnetic field[7] and the problem of separating the electronic and nuclear motions in the theory of molecules and solids.[8] We use the same sort of adiabatic approach that has proven useful in the latter two problems.

Let us write the Hamiltonian in the form

$$H = H_0 + H_1 \tag{3}$$

where

$$H_0 = - \gamma \frac{\partial^2}{\partial z^2} + \frac{\delta}{z} + x\mathscr{E}z \ , \quad z \geq 0 \tag{4a}$$

$$H_1 = - \frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} + U(\vec{r}) \ . \tag{4b}$$

Let the eigenfunctions of H_0 be denoted by $f_\lambda(z)$. In the present paper we assume that the wave function $\psi(\vec{r})$ consists of a product

$$\psi(r) = \chi^{(\lambda_0)}(x,y) f_{\lambda_0}(z) \tag{5}$$

where $f_{\lambda_0}(z)$ is the electric sub-band wave function of lowest energy. For $f_{\lambda_0}(z)$ we choose the variational form of Fang and Howard[9]:

$$f_{\lambda_0}(z) = (b^3/2)^{\frac{1}{2}} e^{-bz/2} z \ , \quad z > 0. \tag{6}$$

For the lowest sub-band λ_0, there is a series of bound states. We shall discuss the ground state and the lowest excited states that are coupled to the ground state by electric dipole transitions.

The overall wavefunctions for these states have the symmetries of hydrogenic $2p_0$ and $3d_{\pm 1}$ states, respectively. For these states, we choose the $\chi^{(\lambda_0)}(x,y)$ to have the variational forms

$$\chi_{2p_0}^{(\lambda_0)}(x,y) = (a_2^2/2\pi)^{\frac{1}{2}} e^{-a_2\rho/2} \tag{7a}$$

$$\chi_{3d_{\pm 1}}^{(\lambda_0)}(x,y) = (a_3^4/12\pi)^{\frac{1}{2}}(x \pm iy) e^{-a_3\rho/2} \tag{7b}$$

where $\rho = (x^2 + y^2)^{\frac{1}{2}}$.

In the spirit of the adiabatic approximation, one would determine the parameter b by minimizing the expectation value of H_0. We shall generalize the situation by determining all variational parameters through minimizing the expectation value of the total Hamiltonian H. This procedure leads to different values for b for the $2p_0$ and $3d_{\pm 1}$ states which we designate by b_2 and b_3, respectively.

III. RESULTS

   A.   Energies

   The evaluation of the expectation values, E_{2p_0} and $E_{3d_{\pm 1}}$, is straightforward. The values of the variational parameters a_i, b_i in each case were obtained from the equations

$$\frac{\partial E_{2p_o}}{\partial a_2} = \frac{\partial E_{2p_o}}{\partial b_2} = 0 \qquad (8a)$$

$$\frac{\partial E_{3d_{\pm 1}}}{\partial a_3} = \frac{\partial E_{3d_{\pm 1}}}{\partial b_3} = 0 \qquad . \qquad (8b)$$

In order to obtain the binding energies, we must obtain the expectation value of the Hamiltonian without the impurity term. It is sufficient to consider the Hamiltonian H_o given by Eq. (4a). We use the variational trial function given by Eq. (6). The expectation value of the Hamiltonian H_o calculated with this trial function is given by

$$E_s = \frac{1}{4} \gamma b^2 + \frac{1}{2} \delta b + \frac{3 \mathscr{C} \varkappa}{b} \qquad (9)$$

from which one determines the optimum value of b by minimizing E_s. From the minimized values of E_{2p_o}, $E_{3d_{\pm 1}}$, and E_s, the binding energies are calculated from the equations

$$E_{2p_o}^B = E_s - E_{2p_o} \qquad (10a)$$

$$E_{3d_{\pm 1}}^B = E_s - E_{3d_{\pm 1}} \qquad (10b)$$

We have calculated the variational parameters and the binding energies for the $2p_0$ and $3d_{\pm 1}$ states for electric fields ranging from zero up to 10^{10} esu. The results are tabulated in Table I. The binding energies are plotted as functions of the electric field in Fig. 1. We see that the binding energies increase monotonically with increasing electric field and approach asymptotic limiting values at very large fields. The limiting values at high fields correspond to the binding energies of two-dimensional hydrogen-like atoms. The binding energies of the $2p_0$ and $3d_{\pm 1}$ states increase by factors of over ten and four, respectively, from zero field to very high fields. Associated with the increases in binding energies are decreases in the effective Bohr radii in the plane of the oxide-semiconductor interface. The effective Bohr radii are inversely proportional to the variational parameters a_2 and a_3 and decrease by factors of over four and two in going from zero field to very high fields for the $2p_0$ and $3d_{\pm 1}$ states, respectively.

We have also calculated the binding energies as functions of the distance of the impurity from the silicon-oxide interface when the impurity is in the oxide. The results are given in Figs. 2 and 3 for several electric fields. We see that the binding energies decrease with increasing distance of the impurity from the interface.

IV. DISCUSSION

In our previous paper[5] on this subject, we employed the variational trial functions of Karpushin[1] and Bell et al[2] to investigate the effect of an electric field normal to the SiO$_2$ - Si interface. These trial functions do not have the form specified by Eq. (5) and do not give the correct limiting values for the binding energies at high fields - namely, 4.0 Ry* for the 2p$_o$ state and 0.444 Ry* for the 3d$_{\pm 1}$ states. The trial functions used in the present paper, on the other hand, give the correct limiting values of the binding energies.

These limiting values are the binding energies of the appropriate states of a two-dimensional hydrogen-like atom. It should be noticed that the two-dimensional value is closely approached for the 2p$_o$ state only at very high electric fields in the 10^9 - 10^{10} esu range. Such fields are in fact not realizable in the SiO$_2$ - Si system since the energy barrier between the SiO$_2$ and Si is only ~3 eV. Physically achievable fields may reach as high as 10^3 esu (3 x 10^5 volts/cm) where the 2p$_o$ state binding energy is intermediate between the two-dimensional and three-dimensional limits. Thus, the use of the two-dimensional binding energy in discussing the properties of inversion layers may be somewhat misleading.

The calculations reported in this paper are based on a number of simplifying assumptions. We have already alluded to our use of an infinite potential barrier at the SiO$_2$ - Si interface. It would be desirable, particularly at the higher electric

Let us now compare our theoretical results with the experimental results of Hartstein and Fowler[6] who have measured the conductivity of n-channel silicon MOSFET devices in which Na^+ ions were diffused through the oxide to the oxide-semiconductor interface. Over a certain temperature range, the peak conductivity can be described by an activation energy which Hartstein and Fowler identify as the binding energy of an impurity band. This binding energy for the case of a narrow impurity band should be identifiable with the binding energy of an isolated impurity that we have considered in the present paper. By varying the substrate bias Hartstein and Fowler were able to vary the electric field in the inversion layer and thus were able to study the activation energy as a function of electric field. They found that in a sample with 5×10^{11} cm^{-2} oxide charge density the activation energy varied from 18 meV at zero substrate bias to 25 meV at -15V substrate bias. The corresponding electric fields are estimated to be 19.9 esu and 60.4 esu, respectively. From Fig. 1, we see that our calculated binding energies for the $2p_0$ ground state at these two electric fields are 0.50 and 0.60 Ry^*, respectively, or 21 and 25 meV, respectively. Thus, our theorectical results agree rather well with experiment.

In fact, the good agreement with experiment is probably fortuitous because of the many approximations we have made. For example, the impurity ions are not exactly at the interface, and the interface itself is not a geometrical plane as we have

fields, to use a finite barrier of ~ 3 eV. One would then have to allow penetration of the electron into the oxide. In the present work we have assumed that the impurity ion is located exactly at the interface. In an experimental situation, however, the impurity will, in general, be situated at some finite distance from the interface. This possibility is taken into account in the Stern-Howard formalism and is currently being investigated by detailed calculations. Another point which should be raised is that the interface is not a mathematical plane, but in fact is a somewhat diffuse entity extending over a region of 5 - 10A.[10] This might be taken into account by using a position-dependent dielectric constant which varies smoothly from the value for silicon to that for SiO_2 across the transition region. Another assumption which we have made is to ignore the presence of the constant energy ellipsoids whose major axes are parallel to the interface. Taking into account these ellipsoids would lead to additional, higher lying, bound states and some modification of the bound states already considered due to intervalley coupling. We have also assumed that the electric field due to the inversion layer is a constant, whereas, in reality, this is not so. Nevertheless, the work of Stern and Howard[3] indicates that the variation of the electric field over the dimension of a bound state is rather small. Finally, we note that our use of the effective mass approximation may lead to some error, particularly at the higher electric fields where the bound state wave functions are compressed very close to the interface.

assumed. We have neglected whatever screening and impurity banding are present in the experimental situation. Also, at the relatively low electric fields in the experiments, our variational wave function can probably be improved. All of these aspects are now being investigated.

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TABLE I. Variational parameters a and b and binding energy E^B for the $2p_0$ and $3d_{\pm 1}$ states as functions of electric field $\mathcal{E}$. The units are indicated in parentheses.

$\mathcal{E}$(esu)	$2p_0$			$3d_{\pm 1}$		
	$a(1/a_0^*)$	$b(1/a_0^*)$	$E^B(Ry^*)$	$a(1/a_0^*)$	$b(1/a_0^*)$	$E^B(Ry^*)$
1	0.91	1.64	0.38	0.60	0.69	0.14
10	0.93	1.72	0.46	0.67	0.89	0.20
10^2	1.05	2.20	0.66	0.83	1.59	0.27
10^3	1.34	3.80	1.01	1.04	3.37	0.35
10^4	1.78	7.68	1.51	1.20	7.40	0.41
10^5	2.29	16.34	2.11	1.29	16.20	0.44
10^6	2.81	35.26	2.70	1.32	35.19	0.44
10^7	3.25	76.16	3.20	1.33	76.12	0.44
10^8	3.57	164.4	3.55	1.33	164.4	0.44
10^9	3.84	354.5	3.80	1.33	354.5	0.44
10^{10}	3.88	763.9	3.90	1.33	763.9	0.44

Figure Captions

Fig. 1.   Binding energies versus electric field for the $2p_0$ and $3d_{\pm 1}$ states. The dashed lines are the two-dimensional values.

Fig. 2.   Binding energy of the $2p_0$ state versus distance of the impurity from the interface for several electric fields.

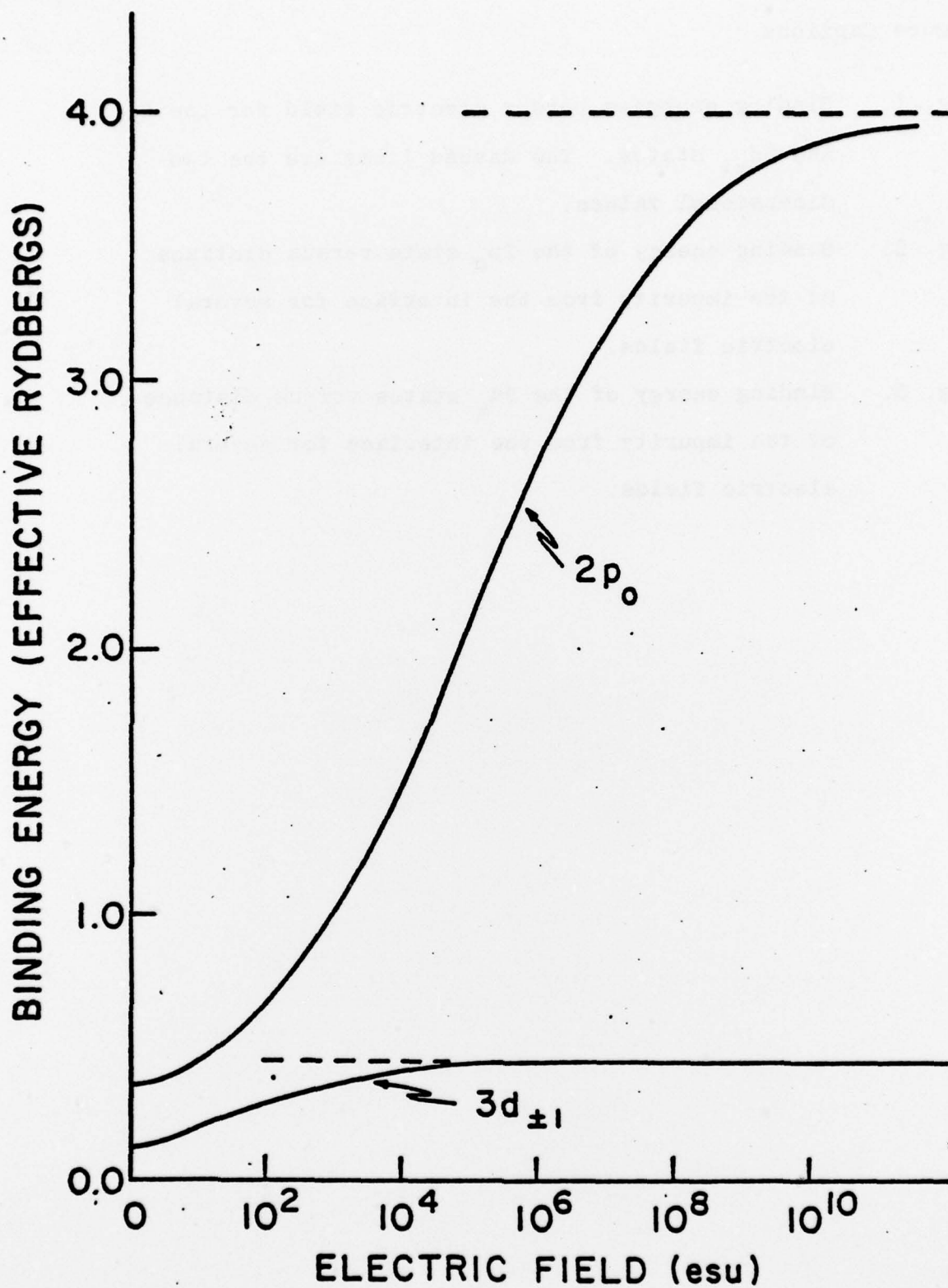Fig. 3.   Binding energy of the $3d_{\pm}$ states versus distance of the impurity from the interface for several electric fields.
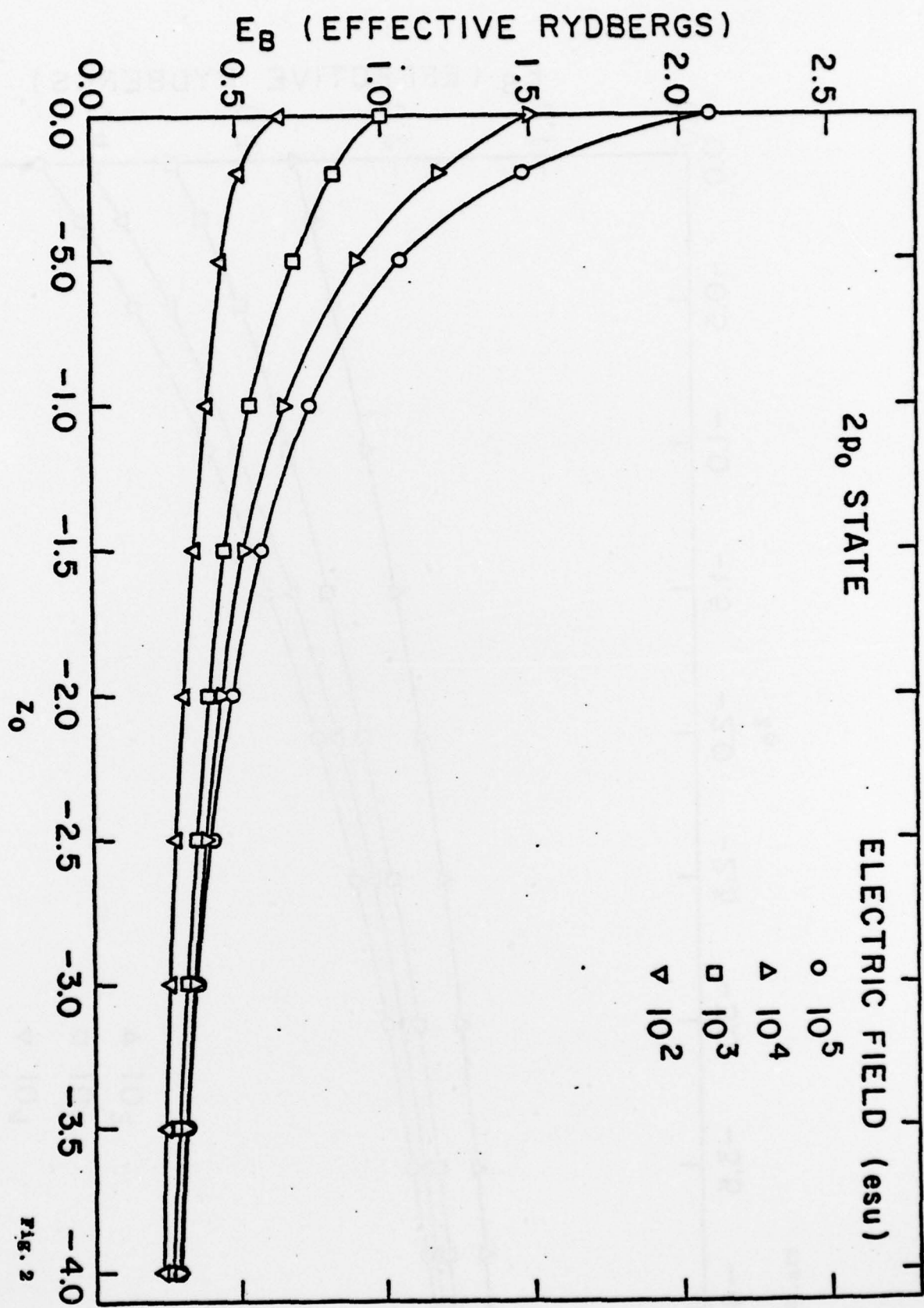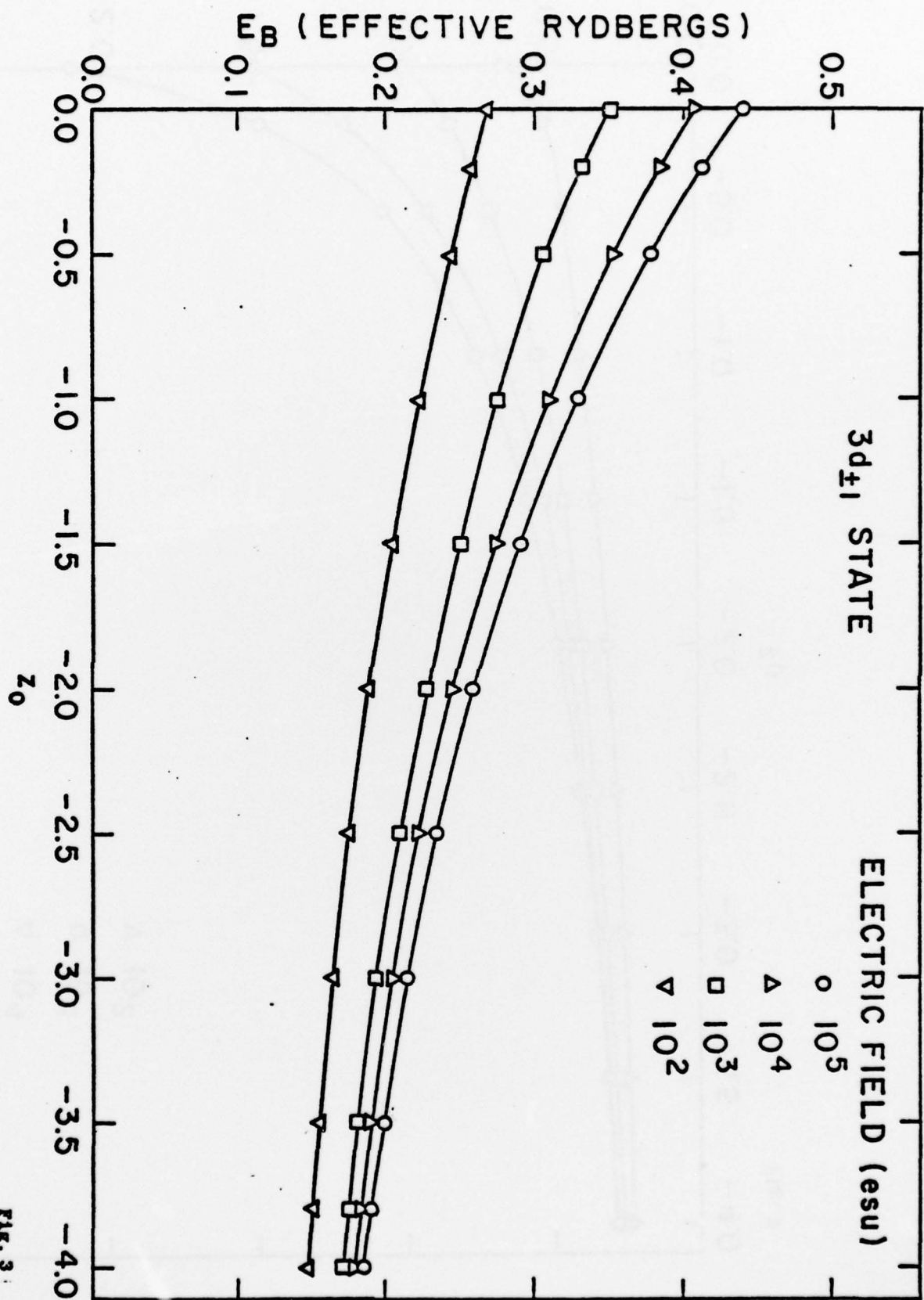
Fig. 1

Fig. 2

Fig. 3

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78